Research and Development

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Project Summary

A Review of Current Methods for Measuring Particulate Matter Including Condensables from Stationary Sources

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The PM₁₀ ambient air particulate concentration standard has created a need for updating measurement methods for PM₁₀ emissions (nominally 10 µm aerodynamic diameter and smaller) from stationary sources. Condensable emissions can be a significant portion of stack emissions. Further, since these substances primarily condense to particles less than 10 µm in diameter, they form a greater percentage of the PM₁₀ fraction than of the total particulate matter emissions. Therefore, the need arises for developing a source test method which includes the condensable component of emissions. A review of possible techniques was conducted to determine current methodology and to make recommendations for research. Research is recommended on two approaches. One is a dilution method which simulates plume formation by mixing stack gases with conditioned ambient air; the other is an adaptation of utilizing the Method 5 backhalf catch.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Stationary sources contribute to the ambient particulate burden through three distinct mechanisms. Two are normally considered together as the formation of "primary" particulate emissions from sources, and the third is the formation of "secondary" aerosols, such as sulfates formed from SO₂ and organic smogs formed from photochemical processes. Primary emissions are composed of (1) materials that are in particulate form (solid or liquid) in the gas stream before and after discharge to the atmosphere and (2) materials that are in the vapor phase before discharge but that rapidly condense to the particulate form when they are discharged into and cooled by mixing with ambient air.

Because condensation takes place preferentially on small particles, condensable matter is concentrated primarily in the PM_{10} fraction (particulate matter less than 10 μm in diameter) of source emissions. Since the basis of the standard for ambient air particulate concentrations has been changed from total particulate concentration to PM_{10} concentration, quantitative data on condensable emissions rates will be needed to set up State Implementation Plans for compliance with ambient air PM_{10} standards. However, current methods for particulate emissions measurement usually exclude the condensables fraction.

Efforts are now being made to develop a reference method to quantify the condensables fraction separately from measurements of the particulate portion of primary emissions from stationary sources. In addition, a working definition for stationary sources condensable emissions must be established to develop a reference method. A review of possible techniques was conducted from which recommendations are made for the optimum approach for development of routine field sampling procedures for measuring condensable emissions.

Approaches for Measuring Condensable Matter

To explore the possible options for measuring condensable matter, a working definition of condensable matter is needed. In particular, the quantity of condensable matter that is present can vary because equilibrium vapor pressures and condensation and evaporation rates vary significantly with changes in temperature and other conditions including concentrations. Consequently, the partitioning between the vapor and particulate phases of condensable matter will exhibit seasonal variations. From a regulatory point of view, however, the reference method(s) used for measuring condensable matter should provide results that are not dependent on local temperatures. Thus some standard temperature for sample collection is needed, such as 0, 5, 20, or 25°C. Whatever temperature is designated to be standard, the operational definition of condensable emissions should be that material collected by the selected reference method(s). This type of definition is now used for particulate matter collected by Method 5.

Adaptations of Method 5

In considering the back-half catch as described in Method 5 for further development as a vehicle for collecting condensable matter, certain problem areas must be addressed. A protocol must be devised for carrying out the evaporative process to remove the large volumes of water from the impinger solutions while reducing to acceptable levels any losses of the condensable materials that are to be measured. Because impingers used in conjunction with Method 5 result in vigorous contact between sample gases and impinger solutions, the potential for reactions with gases that could cause positive measurement biases must be eliminated or minimized. Also, impingers may enhance uptake of gases when sampling for condensable materials with Method 5. Research should be performed to determine if these effects occur at a

significant level and to eliminate or minimize them if necessary. Use of a coil-type condenser may reduce these effects. A filter downstream of the impinger/condenser could be used, if necessary, to ensure that no aerosolized portion of the condensate escapes with the spent sample gas.

Dilution Method

In principle, no practical method can be envisioned that would precisely duplicate the mixing process of flue gas with ambient air for all conditions that actually occur However, methods designed to reproduce the important features of the mixing process for some typical conditions have been devised. All involve the dilution of a sample gas stream that has been maintained at or near stack conditions with ambient air that has been conditioned to varying extents. In some cases, the dilution air is simply filtered to remove existing particles. In others, its temperature and humidity are controlled, and in some cases, scrubbing of vapor phase components from the dilution air is done.

Some particulate matter losses occur during transport of stack samples through sampling probes Because the sample must be extracted and transported through a sampling probe to a location outside the stack for a dilution sampling system, the initial size distribution of the particles in the flue gas cannot be duplicated precisely. However, in systems designed to reproduce the important features of mixing the plume with ambient air, these losses are low enough for sufficient quantities of particles in the critical size range (a few hundredths of a micrometer to a few micrometers) to be transported to allow the use of a method involving dilution of an extracted stack gas sample

Research Needs

To help ensure that the most appropriate and acceptable method was recommended, a number of people in regulatory agencies at the state and federal level, experts in source measurement and characterization, experts in the field of pollutant transport and fate, and experts in the field of ambient sampling and analysis were contacted for advice and ideas. The approach preferred by a majority was that of air dilution cooling rather than condensation in impingers or condensers. However, from the standpoint of ease of sampling it was generally agreed that the Method 5 back-half approach would be preferable. Research would be

necessary to resolve the potential, difficulties posed by the large volumes of 1 condensed water and possible reactions of dissolved gases in aqueous solution to form artifacts that could erroneously be counted as condensable matter. Research also would be necessary to develop hardware and establish operational parameters for the dilution train approach. Hence, it is recommended that both the air dilution and the impinger catch approaches be further developed as EPA methods for measuring condensable source emissions. This would not set any precedents in emission sampling methodology because the use of air dilution techniques is already standard in quantifying emissions from mobile sources and from wood-burning stoves, and Method 5 back-half approaches are used in some states.

Working Definition of Condensables

Because the split of any condensable component of emissions from a source between the vapor and condensed phases depends on temperature (and for some compounds, the amount of dilution that has taken place and background concentrations of the material), it is recommended that condensable emissions be defined as the material measured by the sampling train selected by EPA for collecting condensable matter. Primary emissions that include condensable matter would be defined by the catch of the sampling train, inclusive of the nozzle through the filter.

Suggested Dilution Sampling Method

The use of low mixing rates to preserve, insofar as possible, the detailed size distribution characteristics that would develop in the actual plume was not considered to be an important factor by most of the experts who provided advice. By foregoing any attempt to preserve the detailed particle size distribution of the final aerosol, rapid mixing of the incoming sample stream and the dilution air can be used. This permits the design of a compact diluter and keeps the weight and size of the device at a minimum.

Conditioning recommended for the dilution air includes filtration to remove background particulate matter and drying to a dewpoint of 35°F (15°C), with a final temperature of 68°F (20°C). The low dewpoint and moderately high dilution ratio should prevent problems of moisture condensation for most flue

gases that might be encountered.

Because the sample flow is only a small part of the total flow, measurement of the sample flow at the exhaust end of the system, as in Method 5, is not possible in the recommended setup. Instead, a flow-metering element may be installed upstream of the sample inlet to the diluter. A venturi-type flow meter is recommended, but other types might be used

Sampling Protocol

The suggested sampling protocol for a measurement of total emissions including condensable matter parallels that of Method 5 in most respects. A nozzle of appropriate size for the design sampling rate of the system and the gas velocities in the stack would be utilized. A standard Method 5-type traverse pattern would be used in sampling, and the sampling rate would be set according to

the venturi meter readings and adjusted as needed to maintain isokinetic sampling conditions. This protocol does not maintain a fixed dilution ratio, but the variability induced will not pose a problem. A minimum acceptable dilution factor should be specified (which would in turn set a maximum sampling rate); the nozzle size to be used for a traverse would then be selected to ensure that the minimum dilution specification is not violated.

The dilution train will not provide a direct measure of the split between condensable matter and preexisting particulate material in the flue gas unless use of a filter in the train can be developed. However, by running a parallel Method 17 sample, the split could be found by difference

Conclusions and Recommendations

The dilution method appears to be one of two suitable approaches for research and development for measuring total primary emissions including condensable matter from stationary sources. approach forms condensed particulate matter by the same physical mechanism that occurs in actual plumes. Construction of a system with traversing capability that is suitable for field use appears feasible, consequently, this approach is recommended for development. other suitable method is the impinger/condenser approach. This approach requires the least investment in terms of methods development, operator training, and capital equipment costs (because existing equipment may be Research and coincidental adequate). testing should be designed to reveal the relative merits of the dilution and impinger/condenser approaches

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The complete report, entitled "A Review of Current Methods for Measuring" Particulate Matter Including Condensables from Stationary Sources," (Order No. PB 89-169 973/AS; Cost: \$13.95, subject to change) will be available only from:

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